National Gallery Technical Bulletin

Volume 21, 2000

National Gallery Company
London

Distributed by
Yale University Press

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First published in Great Britain in 2000 by National Gallery Company Limited, St Vincent House, 30 Orange Street, London WC2H 7HH

British Library Cataloguing in Publication Data
A catalogue record for this journal is available from the British Library

ISBN 1 85709 251 1
ISSN 0140 7430
525457

Edited by **Diana Davies**
Project manager **Jan Green**
Typeset by **opta**
Printed in Italy by EBS

FRONT COVER
Lorenzo Monaco, *The Coronation of the Virgin* (NG 215, 1897, 216) (detail of Plate 1, p. 44)

TITLE PAGE
Carlo Crivelli, *The Dead Christ supported by Two Angels* (NG 602; detail), after cleaning and restoration

The Discovery and Identification of an Original Varnish on a Panel by Carlo Crivelli

JILL DUNKERTON AND RAYMOND WHITE

THE *Dead Christ supported by Two Angels* (NG 602; Plate 1) was purchased by the National Gallery in 1859, the first of what was to become the largest group of paintings by Carlo Crivelli to be seen in any museum in the world. It came from the Roman dealer Cavaliere P. Vallati, who offered the Gallery the choice of several panels[1] from a partially dismembered polyptych, painted probably in the early to mid-1470s for the church of San Francesco at Montefiore dell'Aso, not far from Fermo.[2] In June 1859 Raffaelle Pinti, an Italian restorer resident in London who often worked for the National Gallery, was paid £10 for 'restoring' the picture.[3] The relatively modest sum and the short time between the panel's arrival and the payment to the restorer indicate that this cannot have been a full cleaning and restoration. Moreover, the painting has suffered two very large losses requiring extensive reconstruction, including gilding. This was almost certainly carried out when it was on the market in Rome. The reconstruction of the missing areas was skilful, but with time the paints used in the restoration darkened – the consequences are most disturbing in the face of the angel on the right – and the nineteenth-century varnish lost its original transparency and became unevenly discoloured.

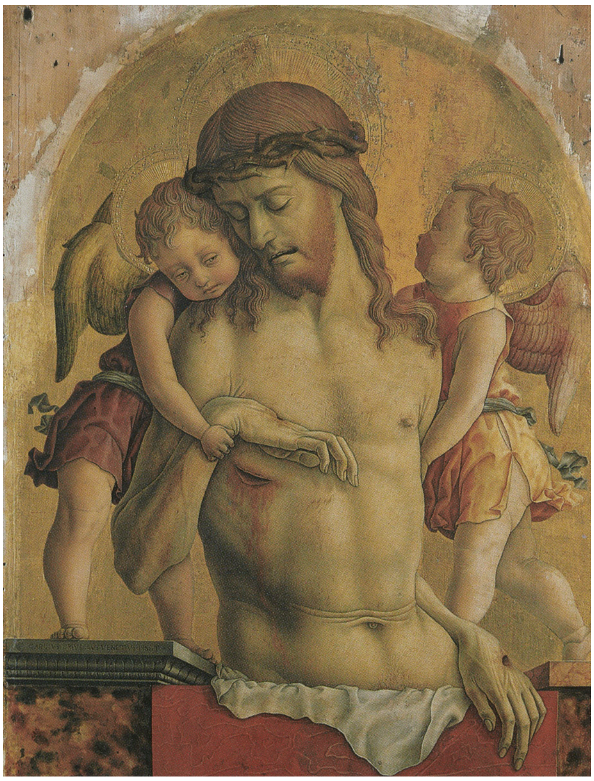


Plate 1 Carlo Crivelli, *The Dead Christ supported by Two Angels* (NG 602), *c.*1470–5. Panel, 75 × 59.5 cm, painted and gilded area 73 × 55 cm. Before cleaning.

Inevitably the large losses presented certain difficulties during the recent cleaning and restoration of the painting,[4] but the treatment has also resulted in a notable discovery. When the painting was examined before cleaning under ultra-violet illumination a substantial layer of varnish with the expected greenish-yellow fluorescence of an aged natural resin varnish could be seen (a patch of this varnish remains immediately below Christ's hand in Plates 2 and 3). On top of it, and therefore showing as black, were several scattered retouchings. These were presumably those made by Pinti in 1859, and analysis indicated that they were executed in dammar, with the addition of a small amount of poppy oil. The varnish was not the usual mastic or dammar found on works restored at the National Gallery in the nineteenth century, but instead contained fir balsam, mixed with a little linseed oil and possibly some pine resin. It seems likely, therefore, to have been applied while the painting was still in Italy. Both varnish and retouchings were readily soluble and could easily be removed.

Underneath was another coating, barely discoloured and with a matt and slightly shrivelled surface. In ultra-violet this exhibits a very different fluorescence, of a warmer more orange-yellow colour. It is applied to the painted areas only, but around the contours the coating has spread a little onto the gilded background. This is most apparent under ultra-violet light, especially along the edge of Christ's torso. The coating must have been applied after the panel had been fitted into the frame since it


Plates 2 and 3 *The Dead Christ supported by Two Angels*. Detail during cleaning, photographed in normal light, and under ultra-violet illumination.

does not cover a strip at the left edge of the parapet.[5] This gives an indication of the effect of the colour of the coating, although it is in fact notably thicker here than over other areas of the painting. In general it is of remarkably even thickness. Everywhere that the paint film is damaged so too is the coating: for example, the abrasions to the paint of Christ's forearm all show as dark in ultra-violet because the fluorescent coating is missing.[6] Conversely, where the coating fluoresces evenly, the paint film is immaculately preserved, above all in the beautifully painted head of the angel (Plate 4). The colours remain unfaded[7] and every last stroke of the finely hatched tempera paint is intact.[8] This, together with the fact that the coating has been applied to the painted areas only, exactly as specified by Cennino Cennini in his instructions on varnishing,[9] gave rise to the supposition that it might be the first varnish to have been applied to the painting, very probably in the fifteenth century, even if not necessarily by the artist himself.

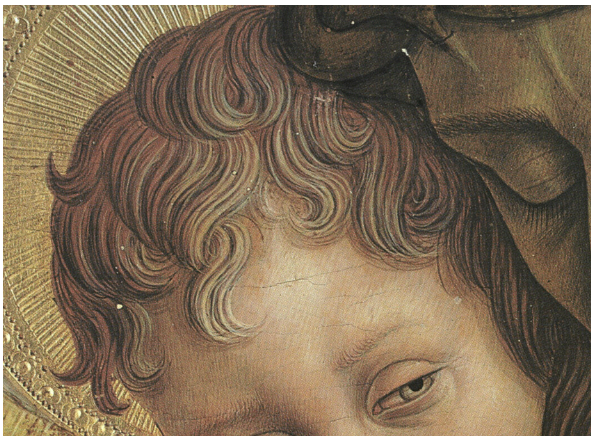


Plate 4 *The Dead Christ supported by Two Angels*. Detail after cleaning, before restoration.

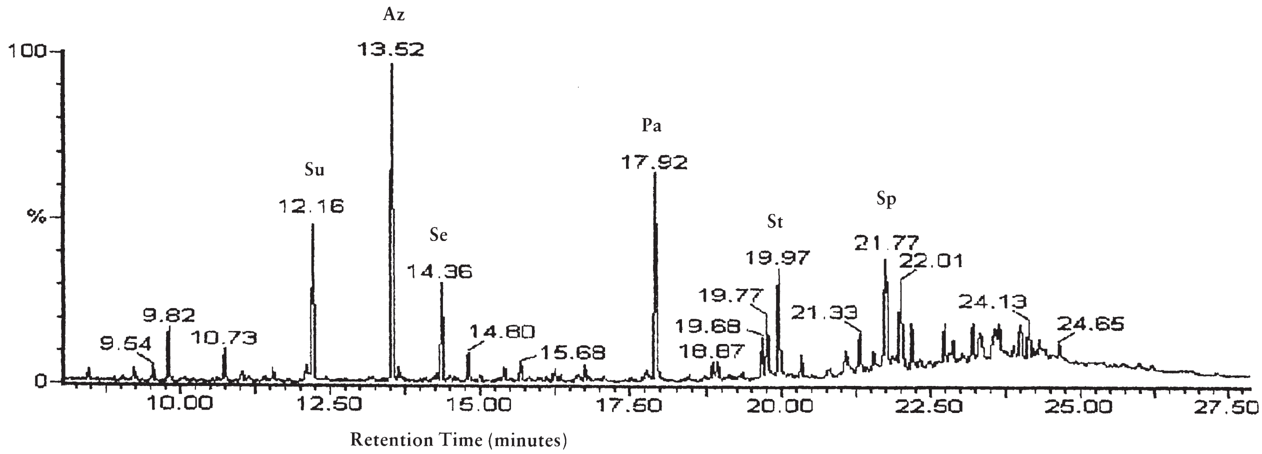


Fig. 1 Total ion chromatogram of original varnish, following thermolytic methylation (see text). Important components include: Su – dimethyl suberate; Az – dimethyl azelate; Se – dimethyl sebacate; Pa – methyl palmitate; St – methyl stearate; Sp – methyl sandaracopimarate. This pattern of components suggests the presence of a heat pre-polymerised walnut oil mixed with an (originally) sandaracopimaric acid-rich resin originating from trees that are members of the Cupressaceae. This family includes *Tetraclinis* as well as *Juniperus* spp. and both produce semi-hard resins, indistinguishable from one another in appearance and properties, which would be classified as sandarac resin.

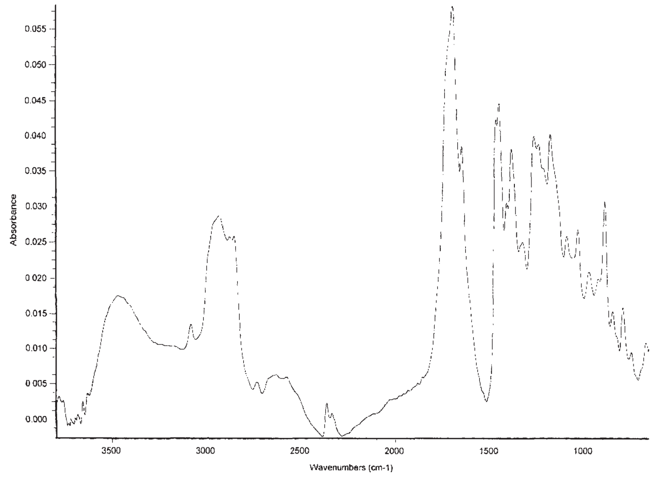


Fig. 2 FTIR spectrum of glassy inclusions in original varnish layer, produced by use of a NicPlan infra-red microscope, employing a Reflachromat x32 infra-red cassegrain objective. Fourier Self-Deconvolution (FSD) has enhanced the spectrum in order to resolve partially overlapping infra-red absorption bands.

The Analysis

Given that most easel paintings of any antiquity have undergone many campaigns of cleaning, prior to the present century, it is rare to have the opportunity of examining an original or early varnish. In the past, abrasives such as powdered glass, sand or pumice, or solutions employing caustic alkali, would have had to be applied to many oleoresinous varnishes, during various campaigns of cleaning over previous centuries. So, having used the severest of cleaning regimes, it is hardly surprising that often little or no vestiges of the original varnish remain. Even when remnants do persist, it is difficult to obtain sufficient monomeric and characterisable organic material to be able to effect a satisfactory identification of the source of the resinous component.

On occasions trapped varnish remnants have been discovered and it has proven possible to undertake an analysis of the residues, with a successful outcome. Such a case was that of an early or original varnish, protected by fitments and revealed during conservation treatment, on a tempera panel attributed to Jacopo di Cione and his workshop, *Pentecost* (NG 578). This was part of the high altarpiece of S. Pier Maggiore, Florence, begun in 1370. Gas chromatography, coupled to mass spectrometry (GC–MS), permitted the identification of the remains of a warm-toned, oleoresinous varnish as a mixture of heat-bodied linseed oil combined with a Cupressaceae resin, namely a sandarac-type resin as mentioned in fourteenth- and fifteenth-century varnish recipes.[10]

In the case of Carlo Crivelli's *The Dead Christ supported by Two Angels* (dated to about 1470–5), sampling was more restricted than in that of the panel from the S. Pier Maggiore altarpiece. The relatively recent varnish layer, sampled from the region of Christ's waist, exhibited some measure of yellowing. Almost certainly this represented an application of varnish, following cleaning, immediately prior to the work's entry into the Collection. Analysis by means of GC–MS, using the method reported earlier,[11] indicated that an oleoresinous varnish containing

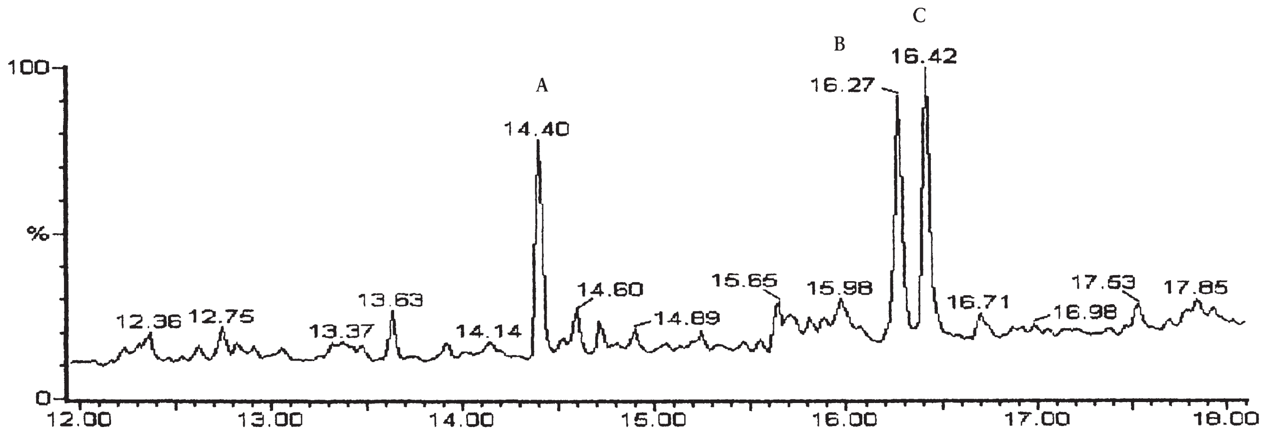
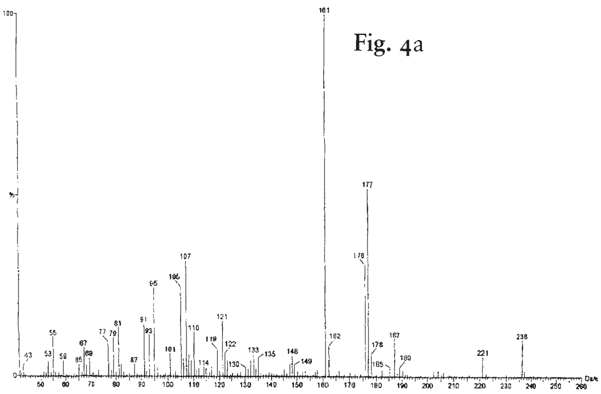


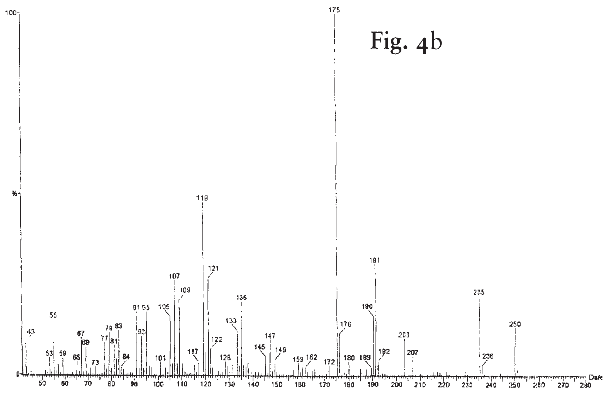
Fig. 3 Total ion chromatogram of carbomethoxydrimane region of glassy inclusions pyrolytically methylated (see text), using a SGE Pyrolysis Unit (furnace type). The diagnostic carbomethoxydrimane fragments generated from the polymer of which these inclusions were predominantly composed are marked by the letters A, B and C. The corresponding electron impact spectra (70eV) are illustrated in Fig. 4 (A, B and C). These correspond to the drimane structures depicted in Fig. 5. The enantiomeric analogues (see Fig. 6), normally appearing approximately 0.6 minutes later – under the conditions employed here – were not detected. We may conclude that this material represents non-incorporated polycommunic acid-rich polymer from a sandarac resin, resulting from incomplete 'running' of the resin.

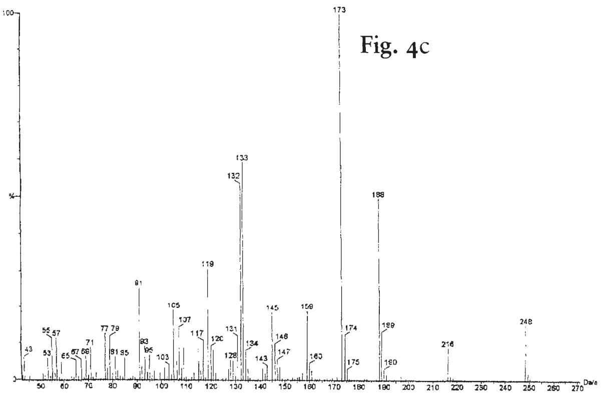
some linseed oil had been used. As mentioned above, the resinous components of this varnish appeared to be a fir balsam, possibly mixed with pine resin and an oleanonic acid-rich triterpenoid resin. Presumably this may have been some form of dammar-like resin. Curiously, though, other dammar components or degradation products – such as ocotillone-types or bisnordammarane keto-lactones – were not evident. There was no indication of the use of mastic resin.

Thermolytic methylation of a sample of the earlier varnish layer, situated directly above grey paint of a sash from the right-hand angel, of a greyish-yellow hue, was carried out using GC–MS. This study revealed the presence of a heat-bodied walnut oil with a resinous component, which exhibited a modest amount of a pimaradiene component, sandaracopimaric acid. This represents the residues of what must have been a sandaracopimaric acid-rich resin, when in a fresh state. In essence, it is reasonable to conclude that this varnish is composed of a Cupressaceae resin, combined with walnut oil, which had been heat-bodied. Careful examination of the chromatogram (Fig. 1) failed to provide any evidence for the presence of dehydroabietic or 7-oxodehydroabietic acids or any of their corresponding hydroxyl compounds. With this in mind, we may rule out the presence of the mixed pimaradiene-rich/abietadiene resins of the subfamily Araucariaceae. Such a resin would be typified by kauri copal from *Agathis australis* Salisbury, only available at the end of the eighteenth century, following the discovery of New Zealand; during the course of the nineteenth century, it was to become much favoured in the production of tough, durable varnish coatings. Moreover, the complete absence of residual traces of dicarboxylic labdanes, such as agathic and the *iso*agathic acids, argues against the inclusion of other copals from Araucariaceous sources, such as the Manila copals (*Agathis alba* (Rumphius) Warburg, otherwise known as *Agathis dammara* Richard).[12] Particularly worthy of note was the absence of diterpenoid labdanes of the enantiomeric series, which are normally the components of the hard copals from the African continent and the New World. Examples of resins from the former include East African or Zanzibar copals, known to have been traded in Europe by the Arabs from before the eleventh century, or those introduced to Europe within the last two hundred years, such as Congo copal and those of Accra and Sierra Leone. Such enantio-labdanes, too, are indicators for the use of both soft and hard South American resins, such as copaiba balsam (soft), from various *Copaifera* spp., and 'copal' from *Hymenaea courbaril* (hard).

Some glassy inclusions within the body of varnish are worthy of discussion. At first it was thought that some local and isolated clumps of these must represent the incorporation of sand or ground glass as an extender or bodying agent or, possibly, as a siccative agent. However, infra-red analysis of such particles unequivocally demonstrated their organic nature and the partially Fourier self-deconvoluted (FSD) spectrum (Fig. 2) compared favourably with that of a polycommunic acid polymer, such as that found in resins exuding from trees that are members of the







Figs. 4a, b and c Electron impact spectra of methylated drimane pyrolysis fragments at 70 eV, for components A, B and C marked in Fig. 3. The molecular ions are 236 Da (A), 250 Da (B) and 248 Da (C).

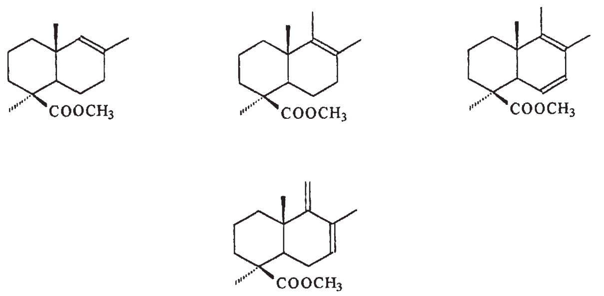


Fig. 5 Structural formulae of carbomethoxydrimanes resulting from 9/11 or 11/12 pyrolytic bond scission of the isoprenoid side chain of polycommunic acid polymers, of the type that may be encountered in sandarac resin.

Cupressaceae subfamily. Apart from some loss in intensity of the *c*.890 cm^{-1} exocyclic- methylene band and an increase in overall carbonyl content, much as would be expected in an old sample, a polycommunic acid polymer basis seems most likely. This lends additional support to the principal evidence from GC–MS analysis of the residual monomeric indicators. These inclusions appear to result from ground sandarac resin that has not been sufficiently heated to cause scission of the polymer and decarboxylation (so somewhat reducing polarity of the oligomers) to have permitted homogeneous incorporation of the resin particles with the walnut oil. This overall process is termed 'running' and usually involves careful, controlled heating of the resin alone, followed by the addition, with stirring, of hot drying oil. The latter may have already been heat pre-treated or may become heat-bodied during the overall process. Lack of careful control of the heating of the resin can result in resin fines, which end up in suspension and do

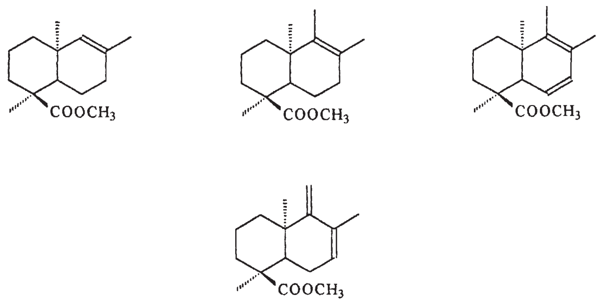


Fig. 6 Structural formulae of carbomethoxydrimanes resulting from 9/11 or 11/12 pyrolytic bond scission of the isoprenoid side chain of polyozic acid polymers, of the type that may be encountered in the hard copals from the Leguminosae trees. Examples include the African and South American copals.

not dissolve in the overall varnish mixture. Equally, excessive heating will result in partial charring or carbonisation of the resin, thereby resulting in a very dark varnish.

Confirmation of this conclusion was afforded by pyrolysis of a crudely separated clump of the glassy particles, in conjunction with *in situ* thermolytic methylation of any carboxylic acid-functionalised fragments so formed. To this end, the clumps of particles were assembled with the aid of a microscope and suspended in 2μL of a 5% methanolic solution of 3-(trifluoromethyl)phenyl trimethyl ammonium hydroxide. This suspension was taken up in a cleaned quartz pyrolysis capillary and pyrolysed at 400° Celsius in a SGE Pyrojector (a pyrolysis unit based on a furnace design), which was continuously flushed with helium gas maintained at a pressure of 8.8 psig above the column head pressure. The chromatogram obtained for this material is displayed in Fig. 3.

Peaks A, B and C were found to possess the spectra that appear in Fig. 4. From their retention times and spectra, we may identify them as carbomethoxylated drimane analogues as depicted in the corresponding sub-figure of Fig. 5. Most importantly, they may be characterised specifically as having a β-methyl substituent at position 10, relative to the plane of the ring. Clearly, they can only originate from the pyrolytic cleavage of either the 9,11 (favoured by the presence of residual allylic isoprenoid side-chains)[13] or the 11,12 bonds of labdane structures falling into the communic acid series, in other words, the sandarac type.[14] The latter series would exhibit β-methyl substituents at position 10 (that is, the ring A/B junction) and the corresponding β-isoprene side chain substituent at position 9.

By contrast, had the polymer been of the ozic or iso-ozic acid type – that is, of the *enantio*-series with both the 10-methyl and the 9-isoprene substituents having α-stereochemistry (with respect to the A/B ring plane) – drimane-related fragments, of the type appearing in Fig. 6, would have been anticipated. They would have been characteristic of the African and New World copals, for example. These enantiomers appear at positions with retention times increased by approximately 0.6 minutes in relation to the corresponding communic-derived analogues. That the polymer had some monomeric diterpenoid units incorporated is made clear by the appearance of small amounts of sandaracopimaric acid, liberated in the course of the thermal fragmentation process.

The fact that the sandarac and walnut oil varnish was probably not subjected to prolonged heat may account for its remarkably undiscoloured state. This would explain why it was never removed. Also it may be significant that the panel was on the upper tier of the altarpiece and therefore more inaccessible to early picture cleaners.[15] With increasing refinement of methods of analysis it has become possible to identify thin surface coatings on paintings with much greater precision than before. Nevertheless, the coating found on *The Dead Christ supported by Two Angels* is likely to remain an exceptionally rare example of a very early and, possibly, even 'original' varnish. Its importance is magnified by the fact that it has protected passages of some of the most consummate painting that Crivelli ever produced.[16]

Notes and References

1 When Otto Mündler saw the panel in Rome in May 1858 it was among Vallati's 'lately purchased' pictures by Carlo Crivelli. He noted that 'the execution is delicate; the colouring light in tone and harmonious: state of preservation excellent' (in this he was mistaken). He also commented on two panels from the main tier, the central *Virgin and Child* and the *Saint Francis* (both eventually acquired by the Musée des Beaux-Arts in Brussels) and a predella of Christ with seven apostles, then apparently still a single plank, but soon after cut up and dispersed as single panels. Two of these panels (see below) are now part of the National Trust collection at Upton House. See C. Togneri Dowd, ed., 'The Travel Diary of Otto Mündler', *The Walpole Society*, 55, 1985, p. 233.

2 Six panels from the polyptych remain at Montefiore, transferred to the church of Santa Lucia. For a reconstruction of the altarpiece see P. Zampetti, *Carlo Crivelli*, Florence 1986, pp. 116 and 265–70.

3 This was not recorded in the National Gallery Manuscript Catalogue and therefore not transcribed into the Conservation Record. The payment is among bills in Account Books in the National Gallery Archive. Payments relating to the conservation of paintings and frames have been transcribed by Sarah Perry and we are grateful to her for drawing our attention to them.

4 It is intended to publish an account of the restoration in a future issue of this *Bulletin*.

5 The panels still at Montefiore have retained elements of the original frame.

6 The crown of thorns, completed with oil-containing glazes of copper green, now very discoloured, appears dark under ultra-violet illumination. This is partly because of the effect of the green pigment, but it may be that the varnish did not cover this colour – it would already have been glossy because of the final glaze.

7 Two panels from the dismembered predella of the altarpiece that are now at Upton House, Banbury, have also been cleaned at the National Gallery. It was hoped that the original varnish might be present, but only traces survive, mainly around the contours of the figures and where it has extended onto the gilded backgrounds. There is evidence to suggest that the varnish was removed long before the nineteenth century (when the panels were also with Vallati) and, as a result, colours containing red lake have faded badly. Small areas that were protected by the original frame show that originally the colours were the same as those in the National Gallery panel.

8 GC–MS showed the medium of Christ's white loincloth and the red cloth draped over the parapet to be egg tempera alone. A sample from the dark green (now discoloured to brown) of the marbling contained a little walnut oil in addition to the egg. Since the sample was taken from the edge, which was protected by the frame from the coating, the walnut oil cannot represent contamination of the sample. A little walnut oil was also found with the egg in the dark green paint of the crown of thorns.

9 See Cennino d'Andrea Cennini, *The Craftsman's Handbook*, trans. by D.V. Thompson, Jr, Dover reprint, New York and London 1954, p. 99; and also J. Dunkerton, J. Kirby and R. White, 'Varnish and Early Italian Tempera Paintings', *Cleaning, Retouching and Coatings, Preprints of the Contributions to the Brussels Congress of the International Institute for Conservation*, ed. J. S. Mills and P. Smith, London 1990, 3–7 September 1990, pp. 63–9.

10 Dunkerton, Kirby and White, cited in note 9, pp. 63–9 for historical background, analytical details, discussion and a selection of recipes from the fifteenth century. See also D. Bomford, J. Dunkerton, D. Gordon and A. Roy, with a contribution from J. Kirby, *Art in the Making: Italian Painting Before 1400*, London 1989, pp. 182–5.

11 R. White and J. Pilc, 'Analyses of Paint Media', *National Gallery Technical Bulletin*, 17, 1996, pp. 91–103.

12 Manila copal produced by *Agathis alba* (Rumphius) Warburg, commonly known as the Amboyna Pitch tree, can vary in both colour and transparency and has been classified into three types. These were known by their local names as 'damars': *Damar Merah* (semi-fossilised, light to dark brown lumps from the ground); *Damar Batu* (or *Damar Puti*), pale, clean lumps; *Damar Poeteh*, fine resin collected by incision of the tree's bark.

13 P. W. Atkinson and W. D. Crow, 'Natural and Thermal Isomers of Methyl *trans*- Communate', *Tetrahedron*, 26, 1970, pp. 1935–41.

14 K. B. Anderson, R. E. Winans and R. E. Botto, 'The Nature and Fate of Natural Resins in the Geosphere – II. Identification, Classification and Nomenclature of Resinites', *Organic Geochemistry*, 18(6), 1992, pp. 829–41.

15 The panels that are still at Montefiore were cleaned many years ago by Alfio del Serra. The varnish removal that he carried out was only partial, but he remembers the paint surfaces as being exceptionally well preserved and thinks that they could well have retained some of the original surface coating (personal communication).

16 The fact that Crivelli placed his signature on this panel as well as more conventionally on the main panel of the *Virgin and Child* suggests that he recognised its exceptional quality. The signature, which is under the varnish, has often been doubted in the past (see, for example, Martin Davies, *National Gallery Catalogues, The Earlier Italian Schools*, London 1961, reprinted 1986, pp. 153–4).